

Electrochemistry in Cationic Matrices. Studies of Porphyrins, Phthalocyanines and Metal-Metal Bonded Complexes.

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The electrochemistry of several highly reducible porphyrins, phthalocyanines and metal-metal bonded complexes were investigated in a cationic $4C_8P^+Br^-$ or $4C_8N^+Br^-$ matrix which was deposited as a cast film on a basal plane pyrolytic graphite electrode (BPG) and immersed in aqueous KCl solutions which varied in concentration from 0.01 to 1.0 M. Three series of compounds were investigated. These are: (i) (OEP)FeCl and (TPP)FeCl where OEP and TPP are the dianions of octaethyl- and tetraphenylporphyrin, respectively, (ii) $(SR_4Pc)_2Lu$ and $(SR_8Pc)_2Lu$ where $R = C_{12}H_{25}$ or C_6H_{13} and Pc = the dianion of phthalocyanine and (iii) $Ru_2(F_xap)_4Cl$ and $Ru_2(F_xap)_4(C\equiv CC_6H_5)_2$ where $x = 1, 3$ or 5 and ap = the dianilinopyridinate anion. All of the compounds are characterized by multiple reductions. Those in the groups (i) and (iii) are known to bind carbon monoxide in their electroreduced forms and this reaction was examined both in solution and in the cationic film matrix. Comparisons are made between the film

and solution properties of each investigated compound, both with respect to their electrochemistry and to their ligand binding abilities. All of the redox reactions are easier in the film and occur at $E_{1/2}$ values which are up to 350 mV more positive than half-wave potentials for similar redox reactions of the same compounds in conventional nonaqueous solvents. The potentials are also dependent upon the concentration of KCl and this is discussed in terms of the existing ion-pairing interactions in the film.